USGS

WATER RESOURCES RESEARCH GRANT PROPOSAL

Title: Chromium Oxidation and Reduction Chemistry in Soils: Relevance to Chromate Contamination of Groundwater of the Northeastern United States

Duration: September 1, 1996 to August 31, 1998

Federal Funds Requested $ 58,200

Non-Federal Matching Funds Pledged: $119,108

Principal Investigator.: Brace R. James, Associate Professor of Soil Chemistry.,

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Congressional District: MD 05

Statement of Critical Regional or State Water Problems:

Hexavalent Cr (Cr(VI)) is a Class A human carcinogen that exists in soils and natural waters predominantly as a soluble anion that may form via oxidation of soluble and insoluble forms of nontoxic Cr(III) in soils amended with industrial waste materials. Through this oxidation reaction, a "nonhazardous" waste may create a "hazardous" waste-soil combination that could be a source of Cr(VI) in groundwater. Chromium is a widely-used element in myriad industrial processes, and in the Northeast, actual or potential groundwater contamination by Cr(VI) is a problem near numerous disused industrial waste disposal sites. More than two million tons of chromite ore processing residue (containing both insoluble Cr(III) and soluble Cr(VI)) were used to fill wetlands in the Hackensack River watershed of Hudson County, New Jersey where Cr(VI) now exists at elevated levels in alkaline soils and underlying groundwater. High levels of Cr(III) are found in soils in Massachusetts and Connecticut due to the disposal of tannery and metal plating wastes, respectively, and high levels of naturally-occurring Cr are found in soils derived from serpentinite northwest of Baltirnore, Maryland. It is unknown whether such soils oxidize this Cr(Ill) to Cr(VI) and thereby enrich drainage water in Cr(VI). Oxidation of Cr(III) and reduction of Cr(VI) are reactions that may control the valence state and mobility of Cr at these sites. A knowledge of these soil chemical transformations could be used effectively to predict the mobility of Cr in soil-water systems, and to remediate Cr(VI)-enriched soils via reduction processes that minimize the chances of re-oxidation of the newly-reduced Cr(III).

The EPA and some state environmental protection agencies in the Northeast are engaged in efforts to quantify Cr(VI) in soils, set clean-up standards for Cr-contaminated sites, and devise remediation strategies that will protect human health, ecosystem function, and groundwater quality in the urban areas where these high-Cr soils are found. One key issue that complicates these efforts is the possibility that Cr(III)-to-Cr(VI) oxidation by

manganese (III,IV) (hydr)oxides occurs in soils, a discovery made by Bartlett and James in 1979. Based on this research, regulatory agencies have sometimes assumed that all forms of Cr(Ill) will oxidize to Cr(VI); while at other times, they have assumed that none of it will do so. Because of this situation, reliable, mechanistic information is needed on the possible extent of oxidation of diverse forms of waste and soil-borne Cr(III), on effective remediation-by-reduction strategies, and on assessing soil redox status to predict the valence state stability of Cr. Such information then can be used reliably to predict the solubility and potential mobility of Cr(VI) in groundwater in the long-term. Since the maximum allowable concentration of Cr is 100 micrograms per liter in drinking water (based on total Cr, rather than Cr(VI)), soil redox transformations are pertinent to the chemical composition of groundwater that may be used for domestic water supplies in some locations. In addition, Cr(iII) and Cr(VI) have been identified as "toxics" of concern with respect to ecosystem function and water quality of the Chesapeake Bay.

Statement of results or benefit:

New mechanistic and practical information will be gained from the proposed research through the integration of three initiatives: (1) studies of oxidation of newly-reduced Cr(III), (2) assessments of the efficacy of different remediation-by-reduction processes, and (3) a critical evaluation of new ways of assessing the electron activity and lability in soils enriched with Cr(III) and Cr(VI). The type of information obtained will include knowledge of the rate and extent of oxidation and reduction of different forms of waste-borne Cr(III) and Cr(VI) sampled in the field, as affected by pH and redox status of the soils. This work will be based on studies with selected, redox-active, soluble constituents and with colloidal suspensions. These studies also will be coupled to work with soil materials sampled from the soil profiles at the four locations described above, and brought from the field to the laboratory for study. The new redox assessment work will compare traditional Pt electrode measurements with kinetic evaluations of electron lability and calculations of electron activity based on the analyses of Cr(III), Cr(VI), and other ions in soil solution. While the information will be obtained through basic studies, hypotheses and experimental designs to test them will be developed with the goal of being able to apply the results directly to analytical, regulatory, and remediation concerns pertinent to water quality and soil clean-up in the Northeast region.